

COKING KINETICS OF ARAB HEAVY VACUUM RESIDUUM
BY THERMOGRAVIMETRIC ANALYSIS

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INTRODUCTION

The increased demand for gasoline and heating oil in recent years coupled with the progressively heavier nature of available feedstocks has put a premium on efficient, low cost processes to convert residuum into lighter products. Traditionally, the process of choice has been coking wherein higher molecular weight species are converted to lighter ones by thermal decomposition at elevated temperatures. Coking may be done in either the delayed mode which is a semi-continuous process or in the fluid mode which is fully continuous. Fluid coking results in higher gas and gas oil yields, lower coke production and a higher octane number for the naphtha fraction than delayed coking and is therefore the preferred process to meet current fuel demands. Recent introduction of Exxon's FLEXICOKING process has made this option even more attractive. FLEXICOKING differs from conventional fluid coking in that some of the coke is gasified at $\sim 1800^{\circ}\text{F}$ to produce low BTU fuel gas and has been shown commercially to produce more naphtha and less heavy gas oil than conventional fluid cokers.

Despite these advances, there is still a need to increase the yield of desirable liquids from cokers. This, however, implies an alteration of the basic free radical pathways by which residuum molecules decompose -- pathways which presently are at best poorly understood. In addition, attempts to gain kinetic and mechanistic insight into the thermal reactions involved in residuum conversion are always hampered by the complexity of the feed. The objectives of this study were therefore to (1) determine the coking kinetics of a feed of commercial interest (Arab Heavy vacuum residuum) and (2) attempt to simplify the overall coking kinetics by first separating this feed into subfractions and studying each of these individually. The experimental technique used in this work was thermogravimetric analysis operated in the nonisothermal mode and was similar to that used by others [1-5] for analysis of polymers and oil shale. The emphasis of this study was on the coking kinetics of the whole residuum and its subfractions in contrast to recently published work [6] which focused on the mechanistic aspects of only the asphaltene fraction.

EXPERIMENTAL

The instrument of choice for this study was the Cahn 113 thermogravimetric analyzer (see Figure 1). At the heart of the system is the Cahn 2000 recording electrobalance which has a sensitivity $0.1\mu\text{g}$ and a capacity of 1.0 gram. The sample to be analyzed is suspended from the balance in a platinum pan by a nichrome hangdown wire inside a quartz hangdown tube. The external split shell furnace operates from 100°C to 1100°C and is controlled by microprocessor temperature programmer capable of executing 40 individual programming steps. Programming of the temperature controller (a three mode digital device) provides for automatic variation in gain, reset and rate during operation and insures an extremely linear heating rate up to $\sim 100^{\circ}\text{C}/\text{min}$. The ability to measure the rate

of weight loss is enhanced by the addition of a time derivative computer built into the system which continuously monitors and plots the rate of weight change.

In a typical tga experiment approximately 20 mg of sample was placed into the platinum dish which was in turn suspended from the balance. The glassware was then assembled and the system was pumped down to ~ 0.1 torr, backfilled with dry nitrogen and a constant purge of 38 cc/min helium was passed through the system. The sample was then weighed to determine its initial weight to 0.01mg. The temperature program consisted of ramping from room temperature to 100°C in 5 minutes, holding at 100°C for 10 minutes, ramping from 100°C to 525°C at the desired heating rate and holding at 525°C for 30 minutes. At this point a blend of 80% He/20% O₂ was introduced into the system at ~ 75 cc/min. and the temperature was ramped to 700°C in 20 minutes to burn off the coke. Organic material balances obtained in this manner ranged from 99.5%-100%. The kinetic equations used to evaluate rate parameters are shown in Figure 2.

Arab Heavy vacuum residuum with a nominal cutpoint of 1050°F (565°C) was used as the feed in this study. A portion of this feed was deasphalted with n-heptane; and the maltene (or n-heptane soluble fraction) was then separated into resins and oils on Attapulugus clay [7]. The oils were further separated into aromatics and saturates by the method of Drushel [8] as shown in Figure 3. Analyses of the whole residuum and the resulting four subfractions are shown in Table 1.

RESULTS AND DISCUSSION

Nonisothermal kinetic experiments were carried out thermogravimetrically at heating rates of 1°C/min to 20°C/min. Typical thermograms for the whole feed and each of its fractions at a 10°C/min heating rate are shown in Figure 4. As can be seen, the asphaltenes produce the least volatiles (47.5%) followed by the polar aromatics (82.4%), aromatics (98.6%) and the saturates (99.8%). Weighting of each of these curves by the amount of that fraction separated from the initial feed and summing each of their contributions produced a curve which was very similar to that of the whole residuum.

The asphaltene thermograms were then analyzed to determine the rates of volatilization at various levels of volatile formation (V/V_0). These data were plotted according to equation 4 (Figure 2) and the resulting Arrhenius plot is shown in Figure 5. In agreement with theory, we find straight lines whose slopes can be used to determine activation energies for various stages of asphaltene reaction. In contrast to the oil shale work of Shih [5] who found all of his lines to be of essentially equal slope, we observe a gradual increase in slope (and therefore the activation energy) as a function of reaction, suggesting a change in mechanism, chemistry or both as a function of conversion. Similar plots for the polar aromatic, aromatic and saturate fractions as well as the whole residuum are shown in Figures 6-9 and a summary of the derived activation energies as a function of conversion for all of these fractions is given in Table 2.

It is interesting to note that while activation energies for each of the fractions tend to increase with conversion, only the asphaltenes exhibit such a wide range. It is also interesting that the saturates exhibit a generally higher level of activation energies even though they react more quickly than any other fraction. Finally, we note that the whole residuum seems

to mimic the sum of its parts in that it exhibits fairly low activation energies at low conversions, but has a broad range showing the asphaltene influence at higher conversions.

CONCLUSIONS

We have found that the kinetics of thermal decomposition reactions of a vacuum residuum can be effectively determined by nonisothermal thermogravimetric analysis. Furthermore, separation of the residuum into subfractions before such analysis provides kinetic insight into the behavior of molecules of varying size and chemical composition. Significantly, our results have shown that the activation energies for the coking reactions of all components of the residuum increase with conversion. This suggests that attempts to model residuum coking kinetics using a single activation energy would produce incorrect results; and that it would be more appropriate to use a distribution of activation energies such as that used by Anthony and Howard [9] in coal pyrolysis experiments.

REFERENCES

1. Flynn, J. H. and L. A. Wall, "General Treatment of the Thermogravimetry of Polymers," Journal of Research of National Bureau of Standards, A. Physics and Chemistry, 70A (6), 487-523 (1966).
2. Campbell, J. H.; G. H. Koskinas and N. D. Stout, "Kinetics of Oil Generation from Colorado Oil Shale," Fuel, 57, 372-376 (1978).
3. Campbell, J. H.; G. H. Koskinas; G. Gallegos and M. Gregg, "Gas Evolution During Oil Shale Pyrolysis. 1. Nonisothermal Rate Measurements," Fuel, 59, 718-726 (1980).
4. Campbell, J. H.; G. Gallegos and M. Gregg, "Gas Evolution During Oil Shale Pyrolysis. 2. Kinetic and Stoichiometric Analysis," Fuel, 59, 727-732 (1980).
5. Shih, S. M. and H. Y. Sohn, "Nonisothermal Determination of the Intrinsic Kinetics of Oil Generation from Oil Shale," Ind. Eng. Chem. Process Des. Dev., 19, 420-426 (1980).
6. Cotte, E. A. and J. L. Calderon, "Pyrolysis of Boscan Asphaltenes: Process Description and Nature of Products," Prepr. Div. Petr. Chem., ACS, 26(2), 538-547 (1981).
7. Schucker, R. C. and C. F. Keweshan, "The Reactivity of Cold Lake Asphaltenes," Prepr. Div. Fuel Chem., ACS, 25(3), 155-165 (1980).
8. Drushel, H. V., "Analytical Characterization of Residua and Hydrotreated Products," Prepr. Div. Petr. Chem., ACS, 17(4), F92-F101 (1972).
9. Anthony, D. B. and J. B. Howard, "Coal Devolatilization and Hydrogasification," AIChE J., 22(4), 625-656 (1976).

Table 1

Chemical Analyses of Fractions of Arab Heavy Vacuum Residuum

FRACTION	WHOLE RESID	n-C ₇ ASPHALTENES	POLAR AROMATICS	AROMATICS	SATURATES
WT. %	100.0	23.9	60.3	10.4	5.4
C (WT. %)	83.13	82.65	82.65	84.92	84.93
H (WT. %)	9.79	7.91	9.92	11.91	13.76
O (WT. %)	0.58	0.88	-	-	-
N (WT. %)	0.68	1.18	0.56	<0.3	<0.3
S (WT. %)	5.71	7.51	5.45	2.41	0.016
(H/C) _{AT}	1.41	1.15	1.44	1.68	1.94
\bar{M}_n (TOL., 50°C)	~2500	~7500	~1900	~900	~900
C _A (MOLE %)	-	48.4	39.7	35.4	-

Table 2

Calculated Activation Energies
for Arab Heavy Vacuum Residuum and Fractions

FRACTION OF TOTAL VOLATILES	ACTIVATION ENERGY (KCAL/MOLE)				WHOLE RESID
	ASPH.	POLARS	AROMATICS	SATURATES	
0.2	42.1	37.6	36.3	40.4	36.8
0.4	43.2	37.9	41.3	38.7	42.9
0.6	51.0	40.0	44.3	44.6	45.9
0.8	67.2	43.5	43.6	51.7	49.9
0.9	80.5	45.6	46.8	52.9	60.5

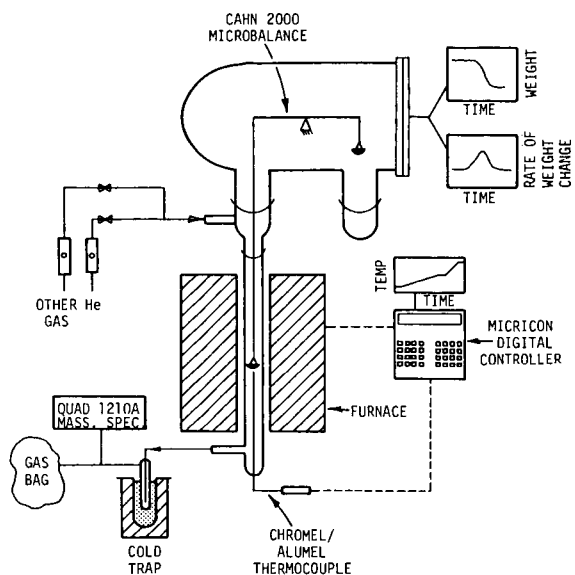
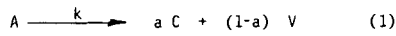


Figure 1. Schematic of Thermogravimetric Analysis System



$$\frac{dV}{dt} = (1-a)kA \quad (2)$$

$$\frac{1}{V_0} \frac{dV}{dt} = k_0 e^{-E/RT} (1-V/V_0) \quad (3)$$

$$\ln \left(\frac{1}{V_0} \frac{dV}{dt} \right) = \ln k_0 + \ln (1-V/V_0) - E/RT \quad (4)$$

Figure 2. Kinetic Model Used in Coking Study

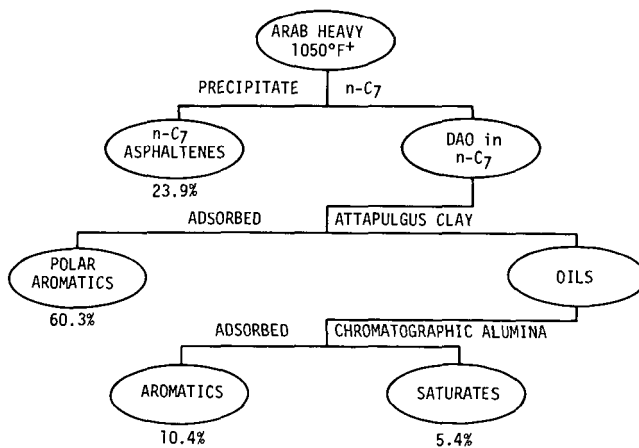


Figure 3. Residuum Separation Scheme

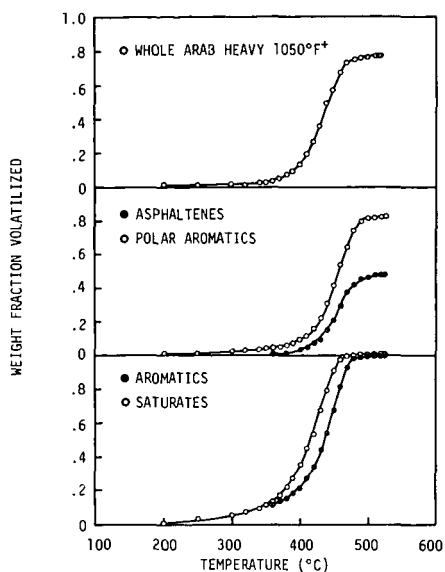


Figure 4. Volatile Evolution from Arab Heavy Vacuum Residuum and Fractions at Heating Rate of 10°C/min

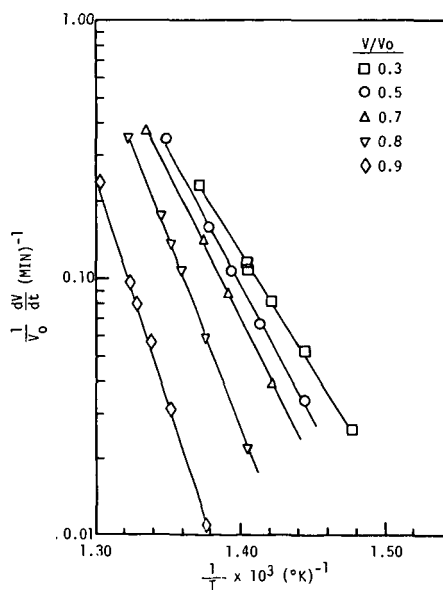


Figure 5. Arrhenius Plot for Asphaltene Fraction

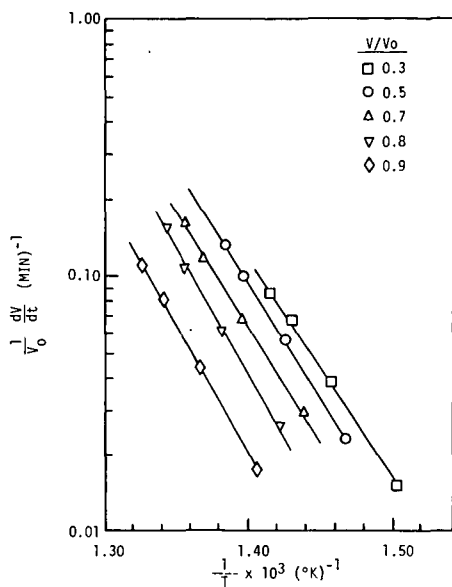


Figure 6. Arrhenius Plot for Polar Aromatic Fraction

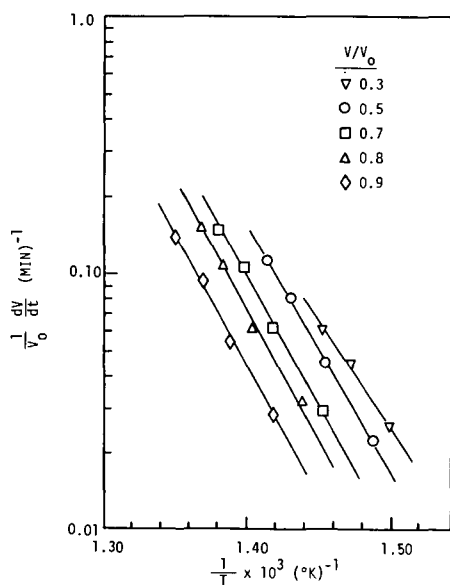


Figure 7. Arrhenius Plot for Aromatic Fraction

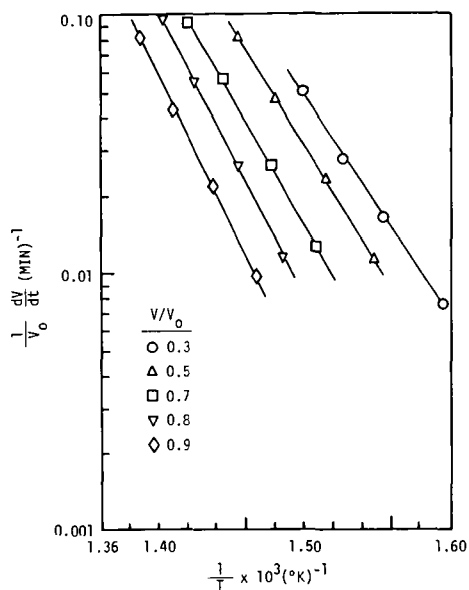


Figure 8. Arrhenius Plot for Saturate Fraction

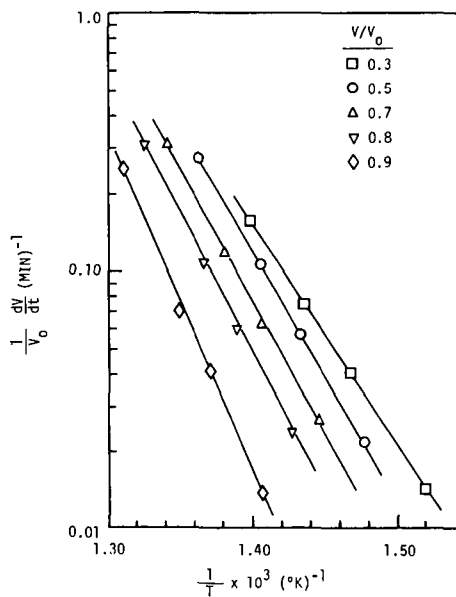


Figure 9. Arrhenius Plot for Whole Resid